Mesodynamical Simulations with Quantum Mechanical Description of the Thermal

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We have recently developed new equations of motion for particle-based mesodynamics simulations that lead to a thermodynamically accurate description of the energy exchange between explicit (mesoscopic) and implicit degrees of freedom (DoF). In a mesodynamical description one describes groups of atoms (molecules or crystalline grains) with a single mesoparticle. The new mesodynamics equations of motion:

$$\dot{r}_i = u_i + \chi_i F_i$$
$$\dot{u}_i = \frac{F_i}{m_i}$$
$$\dot{E}_i^{\text{int}} = \frac{\dot{T}_i^{\text{int}}}{C_i^{\text{int}}} = \chi_i F_i \cdot F \qquad (1)$$

where $\chi \propto \gamma\,(T_i^{ext} - T_i^{\text{int}})/T_0$, T_i^{ext} and T_i^{int} are the external and internal temperatures, respectively, C_i^{int} is the specific heat of the internal DoFs, and γ determines the characteristic time of the coupling between internal and explicit modes.

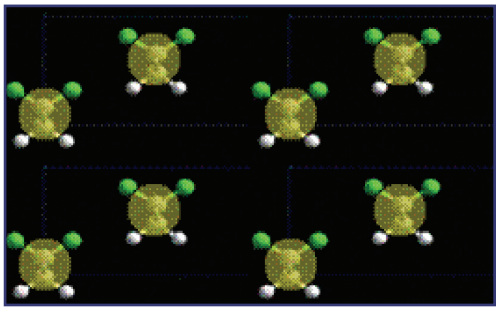


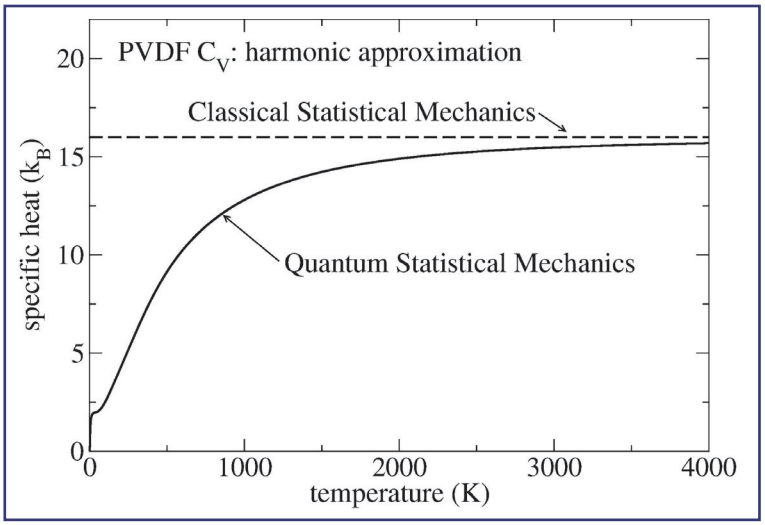
Figure 1— All-atom and mesoscopic representation of the PVDF crystal. Each mesoparticle represents a polymer chain.

The new mesodynamics description satisfies the following desirable properties:

- total energy (mesoparticles plus internal DoFs) and center-of-mass velocity of the system are conserved,
- exchange of energy is done on a spatially local basis,
- implicit DoFs are described by their specific heat that can be calculated from first principles enabling a quantum mechanical description of the thermal role of the implicit DoFs,
- equations of motion are Galilean invariant and the ballistic limit is described correctly, and
- as the coupling between internal and external modes is reduced to zero, Newton's equations of motion are recovered.

In order to validate the new mesodynamics we compare its description of a shockwave propagating in a crystalline phase (denoted β) of the ferroelectric polymer poly-(vinylidene diflouoride) [PVDF, $(CH_2CF_2)_n$] with all-atom molecular dynamics (MD) simulations. We replace each polymer chain with a single mesoparticle (see Fig. 1). We use the classical harmonic approximation to obtain the specific heat of the internal degrees of freedom ($C_i^{\text{int}} = N_i^{\text{int}} k_B$). Our method yields results that are essentially identical to those of all-atom simulations, both in final temperature achieved and in the profile of temperature with distance throughout the shock front.

All-atom MD is classical in nature (in equilibrium and under the harmonic approximation every DoF); thus, the internal specific heat of the polymer molecules is largely overestimated at low temperatures (see upper panel of Fig. 2). The new mesodynamics Eq. 1 naturally enables for a quantum mechanical description of the thermal role of the implicit DoFs. The lower panel in Fig. 2 shows the temperature rise of a thin PVDF slab as shockwaves with particle velocity of 1 and 2 km/s pass through it. As expected, the lower QM specific heat leads to higher temperatures than those obtained under the classical approximation (which are in excellent agreement with all-atom MD). Thus, the new mesodynamics not only provides a computationally more efficient



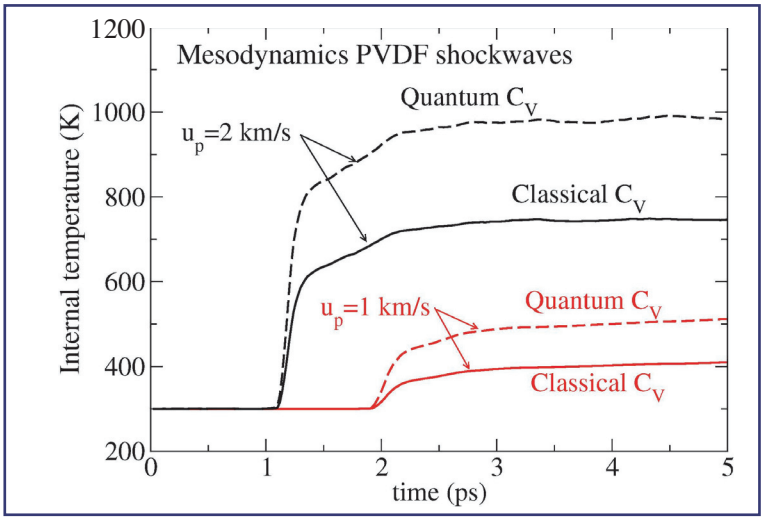


Figure 2—
(Top) Specific heat of the internal degrees of freedom as a function of temperature under the classical harmonic approximation (dashed line) and calculate using QM (solid line). (Bottom) Temperature rise as a shockwave passes through a thin slab of PVDF.

method but also more accurate than all-atom MD.

This new thermomechanical formulation of mesodynamics that describes the exchange of energy between explicit and implicit DoFs is generally applicable to a wide variety of problems in chemistry, biology, materials science, and physics enabling more accurate and computationally efficient particle-based mesoscopic simulations.

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